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NO₂ Suppression of Autoxidation—Inhibition of Gas-Phase Highly Oxidized Dimer Product Formation

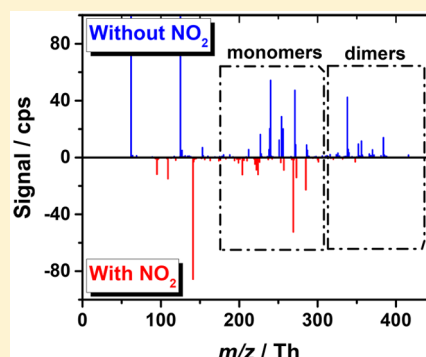
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Supporting Information

ABSTRACT: Atmospheric autoxidation of volatile organic compounds (VOC) leads to prompt formation of highly oxidized multifunctional compounds (HOM) that have been found crucial in forming ambient secondary organic aerosol (SOA). As a radical chain reaction mediated by oxidized peroxy (RO₂) and alkoxy (RO) radical intermediates, the formation pathways can be intercepted by suitable reaction partners, preventing the production of the highest oxidized reaction products, and thus the formation of the most condensable material. Commonly, NO is expected to have a detrimental effect on RO₂ chemistry, and thus on autoxidation, whereas the influence of NO₂ is mostly neglected. Here it is shown by dedicated flow tube experiments, how high concentration of NO₂ suppresses cyclohexene ozonolysis initiated autoxidation chain reaction. Importantly, the addition of NO₂ ceases covalently bound dimer production, indicating their production involving acylperoxy radical (RC(O)OO•) intermediates. In related experiments NO was also shown to strongly suppress the highly oxidized product formation, but due to possibility for chain propagating reactions (as with RO₂ and HO₂ too), the suppression is not as absolute as with NO₂. Furthermore, it is shown how NO_x reactions with oxidized peroxy radicals lead into indistinguishable product compositions, complicating mass spectral assignments in any RO₂ + NO_x system. The present work was conducted with atmospheric pressure chemical ionization mass spectrometry (CIMS) as the detection method for the highly oxidized end-products and peroxy radical intermediates, under ambient conditions and at short few second reaction times. Specifically, the insight was gained by addition of a large amount of NO₂ (and NO) to the oxidation system, upon which acylperoxy radicals reacted in RC(O)O₂ + NO₂ → RC(O)O₂NO₂ reaction to form peroxyacylnitrates, consequently shutting down the oxidation sequence.

KEYWORDS: Autoxidation, Highly oxidized multifunctional compounds, Highly oxygenated molecules, HOM, acylperoxy radicals, dimers, nitrogen oxides, peroxyacylnitrate



INTRODUCTION

Autoxidation of volatile organic compounds (VOCs) is a rapid process by which volatile, gas-phase hydrocarbon precursors rapidly evolve into very low volatile end-products capable of acting as in situ atmospheric aerosol embryos.^{1–5} It is a pseudounimolecular chain of reactions the efficiency of which relies on facile hydrogen abstraction isomerization reactions of the intermediate peroxy radicals (RO₂; see Figure 1). The chain reaction begins with a single oxidant attack forming a carbon-centered radical which rapidly adds an O₂ molecule producing a peroxy radical. If the RO₂ structure is right, that is, if the radical has a loosely bound H atom in the carbon backbone that is about 5 to 8 atoms away from the oxygen atom containing the radical center, the peroxy radical can isomerize by an internal hydrogen abstraction reaction (i.e., H-shift) leading to another carbon-centered radical, and another prompt O₂ addition.^{3,6–8} This forms a hydroperoxyalkylperoxy radical (commonly denoted as OOQOOH) that is potentially able to undergo a second internal isomerization reaction and an O₂ addition. This chain of reactions then repeats until a suitable reaction partner comes along (bimolecular termination), or if through transfer of the radical site the molecule

reaches a structure which is prone to decomposition (unimolecular termination). As the oxidation chain reaction advances, the further H-shifts generally become easier due to addition of oxygen-bearing, electron-withdrawing substituents that loosen the H-binding to the nearest carbon atoms: hence, the term autoxidation—autocatalytic oxidation. Autoxidation is pseudounimolecular in a sense that oxygen addition reactions to carbon-centered radicals are very rapid under ambient atmospheric conditions. Thus, the unimolecular hydrogen shift isomerization reactions of the peroxy radicals constitute the bottlenecks of the oxidation chain.

The oxidation chain is mediated by peroxy radical intermediates and has been observed to complete even in a subsecond time scale.⁵ This oxidation progression has been found especially efficient in ozonolysis of endocyclic alkenes, which often generate peroxy radicals with an aldehyde functionality as the primary oxidation product. Previously, an

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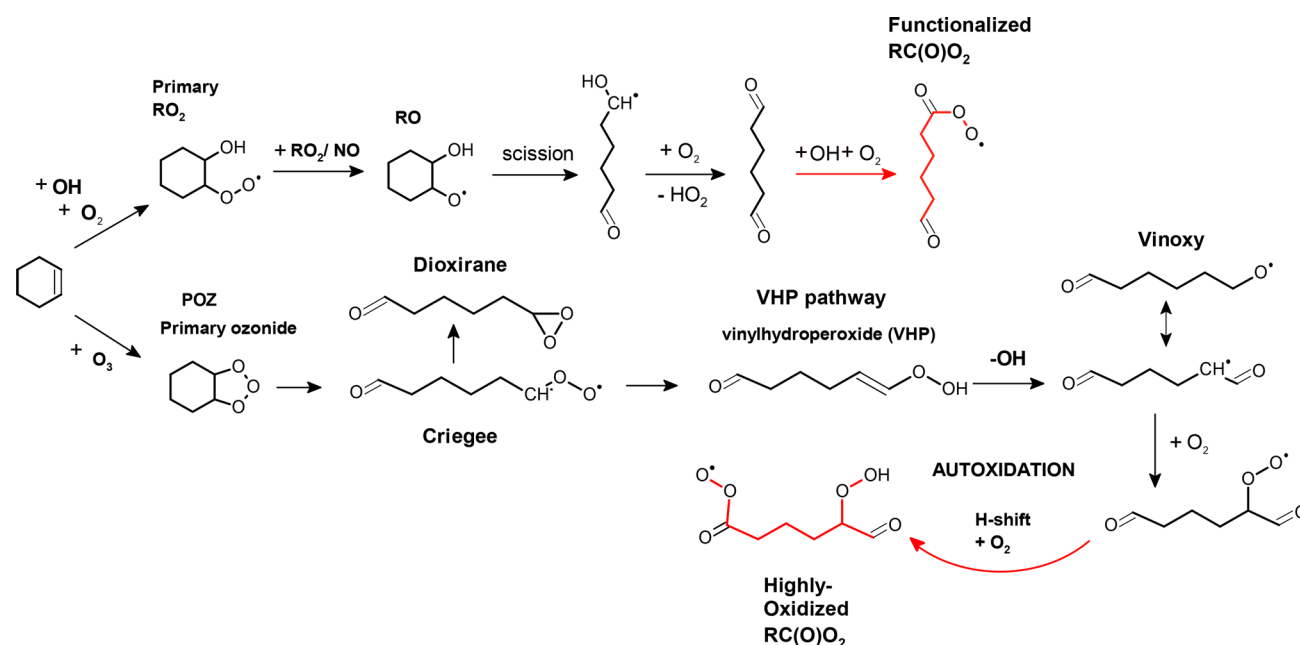
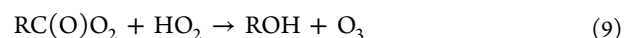
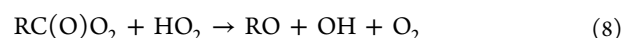
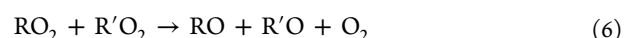
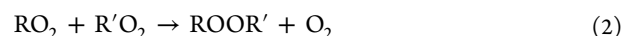
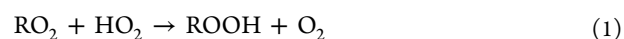


Figure 1. First steps of gas-phase cyclohexene oxidation illustrating the formation of primary acylperoxy radicals ($\text{RC}(\text{O})\text{O}_2\bullet$; in red). Shown are the OH and O_3 initiated oxidation pathways. NO_3 radical and Cl-atom initiated oxidation would likely proceed analogous to OH initiation. Note that the dialdehyde structure is formed in both cases but only the O_3 reaction directly leads to $\text{RC}(\text{O})\text{O}_2$ in pseudounimolecular steps after a single-oxidant attack.

aldehydic 1,4 H-shift rate has been determined at 0.5 s^{-1} for a methacrolein derived RO_2 ,⁹ and larger H-shifts with less strained transition states are likely to be even faster than this. Thus, the looseness of the aldehydic carbon–hydrogen ($\text{C}(\text{O})\text{—H}$) bond provides for a facile first isomerization step, overcoming the bottleneck of the ensuing chain of reactions.² The subsequent autoxidation sequence of a VOC leads to a prompt formation of highly oxidized products that have been found crucial in forming ambient secondary organic aerosol (SOA),¹ even contribute to atmospheric new particle formation.¹⁰ Because of the prevalence of aldehydic functionality in the primary atmospheric oxidation products (see, e.g., refs 3, 11, and 12), the formation of acyl radicals (i.e., radicals with a radical site located at a terminal carbonyl carbon atom; $\text{RC}(\text{O})\bullet$) are currently assumed ubiquitous in autoxidation pathways.

Oxygen addition to acyl radicals produces a special type of a peroxy radical, an acylperoxy radical ($\text{RC}(\text{O})\text{OO}\bullet$; $\text{RC}(\text{O})\text{—O}_2$). Common peroxy radicals (RO_2) are rather unreactive free radicals and are primarily consumed in reactions with other peroxy radicals (RO_2 and HO_2) and with nitrogen oxides ($\text{NO}_x = \text{NO}$ and NO_2) but also in internal isomerization reactions as in autoxidation. These bimolecular RO_2 reactions lead into oxidation chain termination according to reactions 1–5, but also to oxidation chain propagation by reactions 6–8. The termination reactions are composed of hydroperoxide (ROOH) formation with HO_2 in reaction 1, organic peroxide (ROOR) formation with RO_2 in reaction 2, accompanied by carbonyl and alcohol coproducts from reaction 3, organic nitrate formation with NO in reaction 4, and peroxyacynitrate formation with NO_2 in reaction 5. The propagating channels 6 and 7 in reactions with RO_2 and NO have generally high branching factors and lead to very reactive alkoxy radical (RO) generation. Acylperoxy radicals exhibit exceptionally fast rates in all these bimolecular reactions^{12–21} and also show an unusual chain branching behavior in reaction with HO_2 ,

resulting in high yields of oxy radical intermediates (RO and OH) and O_3 production in reactions 8 and 9, respectively.^{22,23} Crucially, the NO_2 reaction 5 is the only reaction that according to current knowledge exclusively leads to oxidation chain termination without a possibility for propagating channels.



As opposed to general primary, secondary, and tertiary RO_2 radical reactions with NO_2 forming unstable peroxyacynitrates (RO_2NO_2) in reaction 5 (i.e., usual gas-phase RO_2NO_2 lifetimes are around 0.1 to 1 s^{11,12,24–27}), the acylperoxy radicals frequently react faster and form considerably more stable peroxyacynitrate ($\text{RC}(\text{O})\text{OONO}_2$; PAN) species, which are known air pollutants and constituents of the photochemical smog and in the atmosphere the main compounds responsible for long-range transport of NO_x ^{28,29} (see Figure 1 for a schematic of acylperoxy radical formation). Previously, acylperoxy radical combination reactions 2 have been suggested to lead to diacylperoxides,^{3,6,30–32} constituting one of the pathways proposed to account for gas-phase organic dimer formation (i.e., products detected with more carbon

atoms than the apparent parent VOC, but not necessarily twice the amount). These dimers have been implied experimentally as especially important for atmospheric new particle formation due to their very low vapor pressures.^{9,33,34} A very recent theoretical work inspecting saturation vapor pressures of modeled highly oxidized product structures found them as the most likely species capable of condensing even onto the smallest of the atmospheric nanoparticles.³⁵ Several other pathways to gas-phase dimers have been proposed, which include, for example, reactions of stabilized Criegee intermediates (sCI) with certain oxygenated VOCs³⁶ and with RO₂.³⁷

Currently the involvement of acylperoxy radicals has only been implied based on theoretical considerations of the reactions propagating autoxidation. Only Berndt et al.⁵ have investigated the moderate addition of NO₂ (around 10¹¹ cm⁻³) to the cyclohexene autoxidation reaction mixture in short reaction time-scale experiments. They reported a single apparent peroxyacylnitrate compound (C₆H₉O₈NO₂) and derived a rate coefficient for its formation of 1.6 ± 0.5 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, without delineating mechanistic insight. Here it is shown by a simple experimental arrangement how NO₂ intercepts the oxidation process and even ceases the oxidized dimer formation completely. This further implies the crucial role of acylperoxy radicals as the mediators of the autoxidation chain, and their nature as the source of the observed highly oxidized dimer compounds. The essence of this work is the realization that whereas RO₂ unimolecular reactions and bimolecular reactions with the common coreagents HO₂, RO₂, and NO can all propagate the oxidation sequence, the NO₂ reaction exclusively leads to termination of the oxidation progression, and thus prevents the HOM and subsequent particle formation processes.

RESULTS AND DISCUSSION

Cyclohexene ozonolysis initiated autoxidation experiments were performed in Quartz flow tube reactors under ambient atmospheric conditions with various concentrations of cyclohexene, ozone, and NO_x and at a 2–20 s reaction time. The setup was similar as used in our previous investigations,^{3,6} and more details of the investigations and the setup are given in the [Supporting Information](#) (SI).

The addition of a large amount of NO₂ into the flow tube gas mixture interferes with the highly oxidized product formation by cyclohexene autoxidation, and most significantly, ceases the dimer formation ([Figure 2](#)). Here, the dimer species constitute all the products observed with more carbon atoms than the parent cyclohexene, that is, a C7 compound would be considered a dimer in this case. This change in the oxidized product distribution is proposed to result mainly from NO₂ reacting with the acylperoxy radical pool forming peroxyacylnitrates (PAN) according to [reaction 5](#), as the common primary (R-COO•), secondary (RC(OO•)R), and tertiary (R₃COO•) peroxy radicals do not generally result in stable reaction products with NO₂ and also have generally slower reaction rates. As shown in [Figure 1](#) (and in [Scheme S1](#)), sequential cyclohexene oxidation inevitably leads to acylperoxy radicals, and offers an ideal system to infer this mechanistic insight.

The most prominent mass spectral peaks observed in the experiments with NO_x addition have been collected in [Table 1](#). The peaks observed without NO_x addition are given in [Table S1](#) of the [Supporting Information](#). Majority of the products were detected as clusters with NO₃⁻, excluding a few

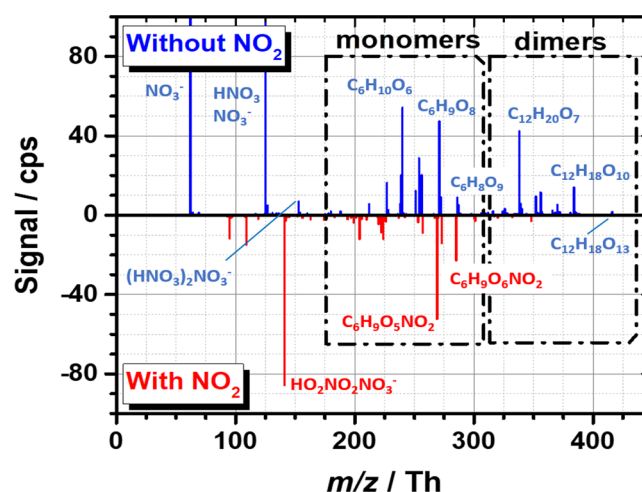


Figure 2. An example of NO₃⁻ chemical ionization mass spectra illustrating the suppression of highly oxidized dimer product formation by NO₂. In the upper panel a spectrum measured in absence of NO₂ (blue) and in the lower panel with a 100 ppb NO₂ addition (red) at a 5.9 s reaction time, are shown.

Table 1. Most Prominent Mass Peaks Measured with NO and NO₂ Addition to the Gas Mixture^a

composition	mass/Th	NO ₂ addition ^b	NO addition ^{b,c}
C ₅ H ₈ O ₄ ^d	^e 194.0306		x
C ₅ H ₈ O ₅	210.0250	x	x
C ₆ H ₈ O ₅	222.0255	x	x
C ₅ H ₉ O ₆	227.0283	x	x
C ₆ H ₈ O ₆	238.0205	x	x
C ₆ H ₉ O ₆	239.0283	x	x
C ₆ H ₁₀ O ₆	240.0361	x	x
C ₅ H ₉ O ₄ NO ₂ ^f	241.0314	x	x
C ₆ H ₉ O ₄ NO ₂	253.0314	x	
C ₆ H ₈ O ₇	254.0154	x	x
C ₅ H ₉ O ₅ NO ₂	257.0263	x	x
C ₆ H ₉ O ₅ NO ₂	269.0263	x	x
C ₆ H ₈ O ₈	270.0103		x
C ₆ H ₈ O ₉	271.0181	x	
C ₅ H ₉ O ₆ NO ₂	273.0212	x	x
C ₆ H ₉ O ₆ NO ₂	285.0212	x	x
C ₆ H ₈ O ₉	286.0052	x	x
C ₆ H ₉ O ₉	287.0130	x	x
C ₆ H ₉ O ₇ NO ₂	301.0161	x	x
C ₆ H ₉ O ₈ NO ₂	317.0110	x	x
C ₆ H ₁₀ O ₅ NO ₃ NO ₂	332.0219		x^g
C ₆ H ₉ O ₉ NO ₂	333.0059	x^g	x
C ₆ H ₁₀ O ₆ NO ₃ NO ₂	348.0168	x^g	x^g

^aThe peaks measured without NO_x addition are given in the [Supporting Information](#) (Table S1). ^b[NO₂] addition was about 400 ppb; [NO] addition was about 200 ppb. ^cNote that the rapid increase of NO₂ in the system potentially enables acylperoxynitrate formation, too. ^dObserved product composition in the spectrum. ^eObserved product exact mass in the spectrum (including the mass of NO₃⁻ of 61.9884 Th). ^fNitrogen-containing products have been marked with italic font and the identical compositions observed in both NO and NO₂ addition experiments have been additionally marked with bold font. ^gSignificantly smaller intensity, but nevertheless present. All masses are given in Thomson units; 1 Th = *u*/*e*, where *e* is elementary charge and *u* is the atomic mass unit.

dicarboxylic acids such as glutaric ($\text{C}_5\text{H}_8\text{O}_4$) and adipic ($\text{C}_6\text{H}_{10}\text{O}_4$) acids, which were also detected as deprotonated product ions (i.e., $\text{C}_5\text{H}_7\text{O}_4^-$ and $\text{C}_6\text{H}_9\text{O}_4^-$, see the SI Table S1). By glancing at Table 1 it becomes immediately evident that NO and NO_2 reactions with oxidized peroxy radicals lead into similar product compositions and exemplifies the ambiguity of simply assigning measured product compositions to certain chemical compounds. The peroxyacylnitrate (and potentially some peroxyxynitrate) compounds observed here could be confused with organonitrates, which are expected to have a significantly different subsequent chemistry; organonitrates formed in reaction 4 are generally much more stable compounds and undergo deposition in the atmosphere, whereas the similar composition bearing peroxyxynitrates (RO_2NO_2) obtained from reaction 5^{11,12,24–27,38} are expected to thermally decompose in a relatively short time frame. In the case of the more stable peroxyacylnitrates ($\text{RC}(\text{O})\text{O}_2\text{NO}_2$), the delayed release of acylperoxy and NO_2 participants constitutes the main long-range transport of NO_x in the atmosphere with the decomposition rate (and thus the distance) heavily influenced by the ambient temperature.^{26,27,39,40}

Whereas NO_2 addition only suppresses the oxidized product formation, NO exerts a more complicated influence. At a low addition level, NO aids the $\text{C}_6\text{H}_8\text{O}_8$ HOM product formation (see Figure S3) by reactive alkoxy radical (RO) formation in reaction 7⁴¹ and illustrates the oxidation enhancing influence of generating highly reactive RO radicals (also possible in reactions 6 and 8^{42–44}). These reactive intermediates enable certain bond breaking reactions⁴³ (e.g., Figure 1) and internal isomerizations⁴² and thus can propagate the oxidation chain reaction, as discussed previously by Kurtén et al.⁴⁴ As the NO reaction can occur multiple times during the oxidation sequence under the present experimental conditions, a later NO reaction can still terminate the oxidation chain by organonitrate formation in reaction 4. Commonly, this is a minor pathway of this type of reaction,¹² but the yield has been observed to increase with the size and functionalization of the R group,⁴⁵ although certain oxidized RO_2 have shown lower yields.⁴⁶ Note that RO can also react with NO and form the corresponding nitrite (RONO) compounds but are not expected to do so due to their very short lifetimes.⁴⁷ If present, however, also they could not be distinguished from other nitrogen bearing compounds due to their perfect mass spectral overlap.

In stark contrast to NO's potentially enhancing influence, the NO_2 reaction does not have any propagating channels, and thus only results in suppression of the oxidation (Figure 2). NO_2 also competes for OH radicals with cyclohexene in this system due to its high concentration and fast reaction at atmospheric pressure (i.e., $k_{298\text{K}}(\text{NO}_2 + \text{OH}) = 1.1 \times 10^{-11,48}$ and $k_{298\text{K}}(\text{cyclohexene} + \text{OH}) = 6.4 \times 10^{-11,49}$ both in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and thereby also suppresses the secondary chemistry in the system. The $\text{OH} + \text{NO}_2$ reaction produces gas-phase nitric acid (HNO_3) to the sample gas flow, which is known to influence the individual detection sensitivities of HOM compounds in NO_3^- CIMS.⁵⁰ Specifically, additional HNO_3 has been shown to favor the highest oxidized species due to their ability to form stronger $\text{HOM}^*\text{NO}_3^-$ clusters,^{50,51} and should thus lead to overestimation of the highest oxidized products. However, the opposite is observed here, as the highest oxidized compounds (e.g., $\text{C}_6\text{H}_9\text{O}_8$ and $\text{C}_6\text{H}_8\text{O}_9$) are

strongly depleted in the obtained spectrum after NO_2 was introduced into the flow.

The complexity of the oxidation progression, even in such a symmetric and simple molecule such as cyclohexene, becomes quickly evident by the subtle changes observed in the product distribution as a function of the initial radical concentration, reaction time, and the amount of NO_x . Both the individual product signal heights and the extent of oxidation were influenced, and a shift from RO_2 radical dominated product distribution at low loadings to closed-shell dominant products at higher loadings was observed (see Figure S5 for changes as a function $[\text{RO}_2]$ and $[\text{NO}_2]$). For example, a moderate NO_2 addition (about 100 ppb) was needed under high $[\text{RO}_2]$ conditions and at a 6 s reaction time for the nitrate peaks to outcompete the pure C, H, O containing HOM product peaks, whereas the highest oxidized closed-shell, monomer species ($\text{C}_6\text{H}_8\text{O}_9^*\text{NO}_3^-$ at 286.0052 Th) was almost lost already at a significantly lower NO_2 addition. At relatively low $[\text{NO}_2]$ and $[\text{RO}_2]$, the oxidation advanced apparently largely unhindered and the highest-oxidized peroxyacylnitrate compounds were observed at 317.0110 Th ($\text{C}_6\text{H}_9\text{O}_8\text{NO}_2^*\text{NO}_3^-$) and 333.0059 Th ($\text{C}_6\text{H}_9\text{O}_9\text{NO}_2^*\text{NO}_3^-$), together with the most prominent highly oxidized radical at 271.0181 Th ($\text{C}_6\text{H}_9\text{O}_8^*\text{NO}_3^-$). Under low $[\text{RO}_2]$ and high $[\text{NO}_2]$, the oxidation was terminated in the early part of the chain and resulted in significantly less oxidized PAN products. These features aptly illustrate the dynamic nature of the autooxidation progression in which the NO_x addition can occur in many instances of the oxidation chain and thus have a significantly different outcome on the specific product formation. To map out the whole product dependencies on the full parameter space (i.e., over concentrations of reagents, oxidants and reaction conditions) is a challenging task and not resolvable with the current mass spectrometric technique lacking structural information but potentially necessary to overcome in the most detailed treatments concerning e.g., specific pollutant mitigation strategies and VOC combustion optimization. The changes observed in the product distribution in this work also potentially imply that the peroxy-H-shift-dynamics even in the cyclohexene system could be yet more complicated than currently thought (as noted recently for isoprene⁵²) and that acylperoxy radicals may be abundant in every ladder of the oxidation progression. Previously Berndt et al.⁵ showed that the RO_2 distribution in cyclohexene ozonolysis is practically fixed already at a 1.5 s reaction time, illustrating the very rapid interconversion of the intermediate peroxy radicals.

The amount of NO_2 required to influence the oxidation sequence will always remain intimately coupled to the structure of the RO_2 being oxidized. Currently the data on $\text{RC}(\text{O})\text{O}_2 + \text{NO}_2$ (and $\text{RO}_2 + \text{NO}_2$) reaction rate coefficients are scarce, and the rates of the large cyclohexene derived RO_2 's can only be estimated at best. In the simplest form, the $\text{RC}(\text{O})\text{O}_2 + \text{NO}_2$ is in competition with the unimolecular initiation of the radical chain reaction, and thus the probability for NO_2 prematurely terminating the sequence is a simple comparison of these two rates (see Figure 3). Typical NO_2 concentrations encountered in the ambient atmosphere usually fall between <0.01 ppb in remote background regions to about few tens to hundreds of ppb found in polluted urban environments with relatively high variability due to localized sources and sinks.⁵³ If the NO_2 reaction rate is estimated by the previously reported prototypical $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and $\text{C}_2\text{H}_5\text{O}_2$ reaction rate coefficients with NO_2 ($k_{298\text{K}}(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 1.5 \times 10^{-11}$

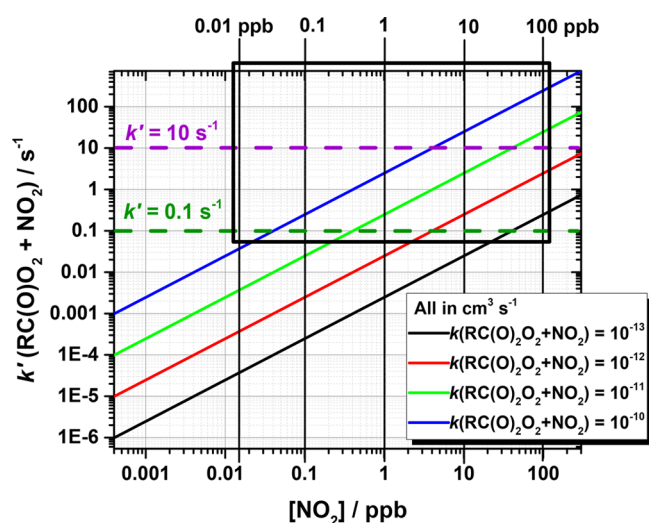


Figure 3. Bimolecular $\text{RC}(\text{O})\text{O}_2 + \text{NO}_2$ reaction rate (in s^{-1}) as a function of NO_2 concentration in comparison to H-shift isomerization rates. At a rate of 0.1 s^{-1} (green dashed horizontal line) autoxidation is expected to compete, whereas at 10 s^{-1} rate (purple dashed horizontal line) the NO_2 reaction will likely dominate. The most common ambient NO_2 concentration range has been marked with a hollow black box.

$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{298\text{K}}(\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2) = 8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁵⁴ then around 0.5 ppb of NO_2 in the case of ethylperoxy radical and 0.27 ppb in the case of acylperoxy can compete with autoxidation rates that are in the order of 0.1 s^{-1} , which is an approximate limit at which autoxidation becomes competitive even under moderately polluted environments.² If compared to the only available experimental determination by Berndt et al.⁵ (i.e., $k = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the needed NO_2 amount is about 2.5 ppb. If, however, the rates for the large functionalized RO_2 are much faster (i.e., $k(\text{RO}_2 + \text{NO}_2)$ close to collision rate of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), then only about 0.04 ppb NO_2 is needed to effectively compete against autoxidation initiation.

In addition to RO_2 's reactions with NO_x , the cross reactions of peroxy radicals become more important with increasing $[\text{RO}_2]$ and reaction time, and thus have implications on

organic peroxide dimer formation (2) and radical pooling (6) in the system. All the experiments were performed in 2–20 s reaction time, during which a shift from unimolecularly dominated chemistry to bimolecularly dominated regime was observed, evident from, for example, significantly enhanced dimer production. Acylperoxy radicals have anomalously fast recombination rate coefficients but also cross combination reactions with other common peroxy radicals (on the order of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$),^{112–21} which increases their contribution over most other RO_2 in the reaction mixture. Previously the cross- and recombination rate coefficients of RO_2 have been reported to span over 6 orders of magnitude and increase in the order: tertiary < secondary < primary < acyl (see, e.g., refs 13 and 55) with the presence of electron-withdrawing oxygenated functional groups close to the reaction center, such as these oxidized RO_2 certainly have, been observed to increase the $\text{RO}_2 + \text{RO}_2$ reaction rates. Several recent experimental studies^{1,3–6,10,41,45} have indicated reaction 2 as the likely source of the observed gas-phase dimer compounds. The current observation of oxidation suppression by NO_2 with concurrent disappearance of dimers (all the dimer compounds observed without NO_x addition decreased by over 95% when sufficient NO_2 (or NO) was introduced into the flow) strongly implies acylperoxy radicals as they key intermediates in the oxidation chain, and likely dimerizing according to reaction 2.

The organic dimer formation by acylperoxy radicals in reaction 2 is in competition with other $\text{RC}(\text{O})\text{OO}\bullet$ loss processes, mainly with the fast-unimolecular reactions of acyl and acylperoxy radicals. Before the formation of acylperoxy radicals occurs, CO-loss from acyl radicals can propagate the radical chain, concurrently converting acyl radicals into alkyl radicals (i.e., $\text{RC}(\text{O})\bullet \rightarrow \text{R}\bullet + \text{CO}$) and accounting for certain products observed with less carbon atoms than the parent VOC.^{3,9,56} Perhaps more importantly, ultrafast hydrogen shift isomerization reactions of the RO_2 can interconvert peroxy and hydroperoxide functionalities (see Figure 4) and has been reported to favor peroxyacids (i.e., $\text{R}-\text{C}(\text{O})\text{OOH}$) over hydroperoxides,^{57,58} with peroxyacids previously identified in the gas-phase cyclohexene oxidation by Iyer et al.⁵⁹ From the current results it is evident that the $\text{RC}(\text{O})\text{OO}\bullet + \text{NO}_2$ reactions are fast enough to compete with the ultrafast H-

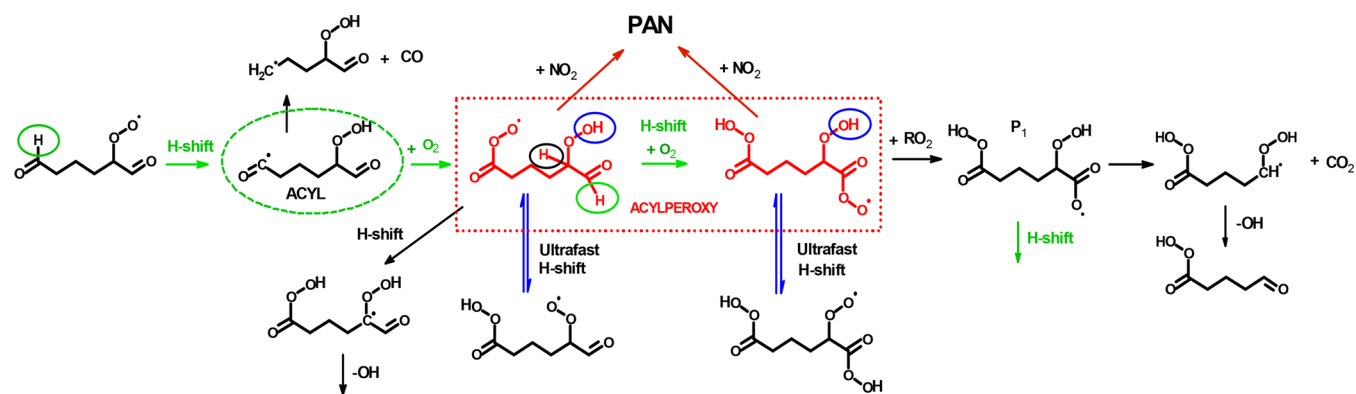


Figure 4. Competing reaction steps in acylperoxy radical formation and subsequent chemistry. As mentioned in the text, post acylperoxy radical intermediates such as P1, an acyloxy radical, could also account for the dimer formation, although oxy radical lifetimes do not generally allow for significant bimolecular reactions except with O_2 . Color coding in the figure: Green arrows show the autoxidation pathway leading to molecular growth, black arrows show inhibition of autoxidation and molecular fragmentation, red arrows show the reactions contributing to PAN formation, and blue arrows show the rapid interconversion of isomers. Acylperoxy radicals have been marked with red color, and the H atoms undergoing H-shifts have been explicitly indicated.

shifts even to overcome them at moderately high $[\text{NO}_2]$, making interception of acylperoxy chemistry possible. Alternatively, the equilibrium between hydroperoxide and peroxy acid functionalities is more even in these highly oxidized RO_2 than previously assumed based on theoretical calculations, making the interception easier. Furthermore, it should be emphasized that for smaller more abundant atmospheric RO_2 s, reaction 6 is far more likely than the dimerization reaction 2, and in the case of $\text{RC}(\text{O})\text{OO}\bullet$ results in acyloxy radicals ($\text{RC}(\text{O})\text{O}\bullet$) and subsequent CO_2 loss.⁴³ However, currently the information on the branching factors of acylperoxy radicals with other peroxy radicals (or with themselves) contributing to reaction 2 versus reaction 6 is scarce,^{12–21} mainly due to the immense difficulty in studying radical–radical reaction product channels in required detail. If the dimer species observed in the current work would be due to other RO_2 s than $\text{RC}(\text{O})\text{OO}\bullet$, they would likely be formed in the postacylperoxy chemistry, as the apparent interception of $\text{RC}(\text{O})\text{OO}\bullet$ by NO_2 ceases the organic dimer formation. On the other hand, it is possible that only acylperoxy radicals have fast enough reactions 2 to contribute significantly to dimer formation in these short reaction time experiments. Regardless of the ultimate reason, these observations imply the special importance of acylperoxy radicals in directing autoxidation phenomena.

Possibilities for misinterpreting the importance of acylperoxy radicals in the current system could result from (i) other oxidized RO_2 s reacting rapidly with NO_2 forming stable nitrates within the reaction time, (ii) certain carbon-centered radicals living long enough to react with NO_2 forming nitro compounds (R-NO_2 , for example, due to longer lifetime of R enabled by equilibrium of the type $\text{R} + \text{O}_2 \leftrightarrow \text{RO}_2$), (iii) stabilized Criegee intermediate (sCI) reactions, $\text{sCI} + \text{NO}_2$, scavenging the prestages of the peroxy radicals before the formation of highly oxidized species occurs, or (iv) that all O_3 is scavenged by NO_2 to form NO_3 , and that NO_3 is not able to initiate HOM formation from cyclohexene. However, (i) only $\text{RC}(\text{O})\text{O}_2$ reactions are known to lead to stable enough products with NO_2 , (ii) strong resonances able to shift the equilibrium to room temperature are most likely absent from the intermediate RO_2 , (iii) cyclohexene ozonolysis does not produce a stabilized CI⁶⁰ to react with NO_2 , and finally, (iv) only a small fraction of O_3 will be consumed under these short reaction times due to the slow $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ reaction,⁶¹ and with such a high $[\text{NO}_2]$ most of the NO_3 will be rapidly converted into N_2O_5 .⁶² Nevertheless, two apparent minor compounds with two nitrogen atoms attached were detected in the high concentration experiments (see Table 1 and Figure S5), which could have potentially formed in NO_3 initiated, and NO_x terminated, cyclohexene oxidation. However, these compositions could also result from product molecules clustering with the reagent ion dimer (i.e., $\text{HNO}_3\text{NO}_3^-$), and although there is currently no possibility to discriminate between either origin the charging by reagent dimer seems far more likely under the current experimental conditions (see the SI for more discussion).

By using mass spectrometric detection methods, it is not generally possible to obtain branching fractions to isomeric products due to their perfect overlap in the mass spectra. Furthermore, the detection sensitivity of different oxidized states is known to differ using chemical ionization as a probing method,^{50,63} increasing uncertainty in using a single calibration factor for all the detected species. By applying this procedure, however, concentrations ranging from fractions of ppt to some

tens of ppt have been reported previously for individual HOMs in cyclohexene autoxidation with the total measured HOM ranging from below one ppt to hundreds of ppt.^{3,5} Yet, it remains unclear how many different acylperoxy radicals there are in the gas mixture, what are their concentrations, and how big a portion of these result in dimer compounds observed in the current CIMS spectra. Nevertheless, it is possible to lean on previous theoretical and experimental foundation on $\text{RO}_2 + \text{NO}_2$ reactions,^{12,24,25,38} and on previous knowledge on cyclohexene autoxidation,^{1,3,5,41,59} to imply the mechanistic details presented in the current work. Cyclohexene ozonolysis initiated autoxidation is a close to an ideal autoxidation system that proceeds largely unhindered due to close-to-optimal structures of the formed intermediates,³ and has a correspondingly high HOM molar yield of 4.8% (average of three determinations with NO_3^- CIMS technique^{1,3,5}). Yet even in this highly efficient autoxidation progression, NO_2 is able to interfere and cuts down the oxidation sequence, preventing formation of the least volatile compounds that would be the most potent in forming ambient particulate matter.^{1,10,35} Just alone substituting the potential peroxy- or carboxylic acid terminal groups into nitrates or peroxy nitrates, as is the case here, constitutes a considerable increase in the resulting product volatility,^{64,65} and corresponding reduction in SOA formation potential. The current finding further suggests that the common procedure of conducting chamber experiments, in which unnaturally high NO_2 concentration is first equilibrated in a chamber environment and then photolyzed to obtain a uniform O_3 concentration (or a suitable NO to NO_2 ratio, or both), poorly reflects the conditions of the true atmosphere. Such an experimental design has the prospective to unintentionally suppress acylperoxy chemistry and thereby also the low-volatile product formation, consequently leading to underestimation of the SOA forming potential of a VOC. Undoubtedly more molecular-level detailed work is required to understand the intricacies of acylperoxy radicals in directing autoxidation pathways.

CONCLUSIONS

Prevention of gas-phase highly oxidized product formation by NO_2 was illustrated in the cyclohexene ozonolysis system, supporting the involvement of acylperoxy radicals as the key intermediates in the autoxidation chain reaction. By addition of NO_2 to the reacting gas mixture, the oxidation pathways were influenced, and the highest-oxidized product signal levels were observed to plummet. Most notably, the dimer formation ceased, which implied that the acylperoxy radicals derived from cyclohexene reacted fast enough with NO_2 and slowly enough unimolecularly that the interception of the autoxidation progression became possible. Furthermore, the NO and NO_2 reactions with the same oxidized RO_2 were observed to lead to indistinguishable product compositions. These observations have consequences on our understanding of the atmospheric oxidation phenomena and exemplify the importance of NO_2 reactions preventing the formation of in situ ambient aerosol precursors. The current finding thus also demonstrates the significance of separating NO_x measurement data into respective NO and NO_2 values as the outcome of a certain VOC oxidation will differ significantly from NO to NO_2 dominated environments, that is, in moving away from primary emission sources. Even more so, this becomes important as the oxidized products are likely to have significantly different chemical nature, yet are not distinguishable from their mass

spectral signals, which is the current primary method for ambient gas-phase aerosol precursor compound detection.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.8b00123.

Methods. Influence of charging probabilities and transmission on measured concentrations. Oxidation pathways. Suppression kinetics. NO_x's enhancing influence. Table S1: Mass peaks measured without NO_x addition. Table S2: Competition of RC(O)O₂ + NO₂ and H-shift reactions. Scheme S1: Further acylperoxy chemistry. Figure S1: Experimental setup. Figure S2: Potential PAN structures. Figure S3: C₆H₈O₈ product formation. Figure S4: Nitrate signals plummeting. Figure S5: NO_x addition at various stages during autoxidation (PDF)

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Notes

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